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(54) PREPARATION AND USE OF PARTICULATE METAL

(71) We, THE DOW CHEMICAL COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Midland, County of Midland, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention pertains to a method of producing metal particulate and more in particular relates to a method of forming metal platelets.

It is known that metal powder, such as aluminium, can be admixed with a carrier material and used in a paint; however, the surface of the painted article has generally been found to have a dull, gray appearance. To obtain a lustrous, generally metallic appearing surface on a substrate, such as a light reflector, a metallic plate is usually applied to the substrate by means of a vapor deposition process.

It is desired to obtain a metallic particulate suitable for, for example, a pigment in a coating composition. Desirably the metallic pigment will form a metallic appearing surface on varied substrates by use of a composition appliable by means such as spraying, brushing, dipping, rolling and the like. The coating composition desirably should be capable of being expeditiously applied to the complex configurations more economically than by vapour deposition.

In accordance with the invention there is provided a method for the preparation of particulate metal which method comprises depositing a metal coating on a substrate by vapor, electroless or sputter deposition and removing the metal coating from the substrate by dissolving the substrate in a solvent therefor, i.e. thickness of the deposited coating being such that upon dissolution of the substrate the metal is released as a plularality of metal particles.

Typically the invention provides generally separated metal platelets of a generally irregular shape usually having a size from 1 to 500 microns. The metal platelets which generally have a largest dimensions, i.e. the length or width, of from 1 to 5000 microns, are suitable for use, as, for example, a pigment in coating compositions or an additive to plastics.

The metal coating may be up to 1000 angstroms in thickness.

The disclosed method preferably comprises providing a substrate which is soluble in a solvent in which a metal deposited thereon is substantially insoluble. At least a portion of the substrate is contacted and plated with the metal or an alloy thereof by means suitable to form metal platelets or flakes upon separation of the metal plate from the substrate. The metal is desirably deposited on the substrate surface to form a metallic coating or plate; such deposition of metal may be within the substrate body. Suitable means of metal deposition are vapor (including vacuum), electroless and sputter processes known to those skilled in the art.

In a particular embodiment of the invention, the substrate is a release layer interposed between the metal coating and a layer of material which is insoluble in the solvent for the substrate.

The substrate may be a silicone resin.

The metal flakes have at least one and preferably two substantially planar surfaces and an irregular periphery. The thickness of such flakes is usually up to 1000 angstroms, advantageously 200 to 1000 angstroms and preferably from 350 to 600 angstroms. Thicker flakes can be employed; however, the visual appearance of the finer coating will not be materially improved over a coating of thinner flakes within the herein-

described preferred thickness range. Preferably the largest dimension i.e. the length or width, of each metal flake is from 1 to 1200 microns. When the flakes are to be added to or admixed with plastics for, for example, molding or coatings, such as brushable, rollable or dipable paints, the largest dimension is preferably from 100 to 1000 microns. Flakes for a sprayable coating preferably have an average largest dimension within the range of 100 to 200 microns. At least one surface of such flake is characterized as visually having a higher luster or shine. In a preferred embodiment, at least one surface of the flake has a specular or mirrorlike, reflective appearance.

Generally, all metals which can be deposited onto a substrate by vapor, electroless or sputter deposition are suitable for use in the instant process. Examples of such metals are Mg, Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, In, Cd, Ag, Pd, Rh, Ru, Mo, Nb, Zr, Y, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Tl and Pb. The metal deposited is preferably Mg, Al, Cu, Au, and Ag. Most preferably aluminium is deposited. As a result herein the term "metal" includes the stipulated base metal and alloys thereof containing greater than 50 weight per cent of the base metal.

After deposition of the metal onto a substrate, such as an organic, metallic or other inorganic shape, film, or sheet, the metal is removed by dissolving the substrate in a solvent. Suitable solvents are those which remove or dissolve the substrate from the metal coating wthout dissolving excessive quantities of the metal.

In one embodiment of the invention, the metal coating is removed from the substrate by contacting at least a portion of the metal coated substrate with a solvent for the substrate and subjecting the solvent and the metal coated substrate to ultrasonic vibration.

When the metal flakes are to be applied to a surface as a reflective layer, additional solvent is generally employed to remove substantially all of the remaining substrate from the individual metal flakes following removal of the coating from the substrate. The cleaned metal flakes can be, for example, dried and stored or introduced into a chemically and physically inert, i.e. non-reactive, material until it is desired to use the metal particulate.

If desired to obtain smaller flakes, the flakes can be subjected to a cutting-type shearing force after removal of the coating metal from the substrate. Such shearing force can be readily applied to a slurry of flakes by means of, for example, the common high-speed kitchen blender.

The so-separated metal flakes are beneficially used as, for example, a pigment in paints, printing inks, organic plastics, automotive finishes and the like. A paint is herein defined as a suspension of particulate pigment in a vehicle with, if desired, a binder and/or color pigment. Binders and coloring pigments are well known in the art. The paint can be expeditiously applied to a surface of simple or complex configuration by means such as spraying, brushing, dipping, rolling, and the like. After application to a surface, the paint can be air dried or cured by conventional means and polished, if desired.

Properly formulated coating compositions with, for example, isopropyl alcohol as a carrier, can be applied to objects formed of polystyrene, acrylonitrile-butadiene-styrene interpolymers, polycarbonates and acrylic plastics. After conventional curing, the adherent coating will have a lustrous, metallic appearing surface.

It has been found that from 0.1 to 10 weight percent and preferably from 0.1 to 5 weight percent of aluminum flake in a vehicle or carrier is sufficient for most purposes. The minimum quantity of pigment that is effective in producing a desired visual appearance of the final coating will vary from application to application. Consequently, the quantity and metals employed in the paint can be varied to economically achieve painted surfaces with differing reflective qualities. For example, a 10 weight percent mixture aluminum flake in toluene or isopropanol has been found to have a paste-like consistency, whereas a 3 weight percent mixture is flowable. Sprayable coating mixtures preferably contain up to one weight percent of the metal particulate. A mirrorlike secondary surface, i.e. a surface in contact with a substrate such as transparent glass, can be obtained by using as little as from ½ to ¾ weight percent of an aluminium particuate in a suitable carrier. Generally coatings applied by brushing or rolling require a higher viscosity than for spraying. This increased viscosity may be obtained by using a greater quantity of metallic particulate for example, about one to about four weight percent.

A combination of flakes of various alloys and metals can also be admixed as a pigment to achieve differing surface characteristics. A surface with a shiny metàllic finish can be achieved by using as little as one gram of metal flakes in a carrier to cover up to 50 square feet (4.6 square meters) of surface. A shiny metallic-like surface can be obtained when as thin a paint layer as 1000 angstroms thick is applied to a clean substrate. Furthermore, an electrically conductive coating on a substrate can be obtained by employing sufficient pigment. An aluminum flake coating composition produced a reflective coating surface

with an electrical resistance of 200 ohms per square.

It is also within the scope of this invention to dissolve the substrate with a solvent suitable for use as at least a portion of the carrier material for the metallic pigment. The pigment containing solvent can then be either added or mixed with the remainder of the paint constituents or used as a paint alone.

The following examples are illustrative of the hereinbefore described method.

EXAMPLE 1

A sheet of polystyrene film 0.3 millimeters thick and weighing 1000 grams was plated with a 450 angstrom thick layer of aluminum by conventional vapor deposition techniques, the plated film was shredded and then mixed in a container with 9500 grams of toluene. The mixture was agitated and in less than 30 minutes the polystyrene was solubilized by the toluene. The aluminum separated as small specular flakes which settled slowly into a loosely packed sediment occupying about ⅓ of the volume in the container. After about 24 hours the clear toluene-polystyrene mixture was removed from the container by decanting. Any remaining toluene-polystyrene mixture was removed by means of a centrifuge.

The separated aluminum flakes were mixed or washed with toluene to completely remove any polystyrene still adhering to the metal. The yield of aluminum flake was 3.3 grams. Each flake observed visually had a lustrous or reflective appearance and was about 450 angstroms thick.

Sufficient toluene was admixed with about 200 milligrams of the washed aluminum flake to provide a flowable mixture containing 0.8 weight percent aluminum solids. This mixture was then mixed with isopropyl alcohol and a solution of ethylcellulose binder and isopropyl alcohol to provide a coating composition with 0.4 weight percent aluminum and an aluminum to binder weight ratio of about 1:1.

The so-prepared coating composition was sprayed by conventional equipment onto a smooth, transparent glass surface in an amount sufficient to coat the equivalent of approximately 30 to 40 square feet (2.8 to 3.7 sq. meters) of glass surface with one gram of aluminum flake. The exposed aluminum coating composition surface had a lustrous, generally metallic appearing surface; however, the coating composition surface in physical contact with the glass, or secondary surface, had an even greater reflectance or mirrorlike surface than the exposed coating surface. When a light with a 5500 angstrom wavelength and a 45 degree angle of incidence was employed, the reflectance of the secondary surface was 72 percent.

EXAMPLE 2

Aluminum flakes were prepared substantially as described in Example 1 and formed into a coating composition containing by weight 0.4 percent aluminum flake, 0.4 percent ethylcellulose, 80 percent isopropyl alcohol and 19.2 percent xylene. The coating composition was sprayed onto a ¼ inch (0.635 centimeter) thick plate glass substrate using an aerosol-type applicator to form an adherent, reflective coating.

As a comparison, a similar ¼ inch (0.635 centimeter) thick plate glass substrate was spray coated, from an aerosol container, with a commercially available aluminum paint. The paint contained 3.3 percent aluminum paste, 9.7 percent processed fish oil and phenolic resin, 50 percent dichlorodifluoromethane and 37 percent xylene.

After air drying, the reflectance of both the aluminium flake containing surface and the comparative aluminum painted surface were compared using visible light and a commercially available Gardner gloss meter. In each reflectance test the meter was standardized to indicate 100 percent for the aluminum flake containing surface. As shown in the following table, the results of the above tests illustrate the superior reflectance obtainable with the aluminum flake containing composition of the present invention.

Angle of Incidence of the Light (degrees)	Surface	Percent Reflectance: Al Flake Containing Coating	Comparative Al Paint
20	primary[1]	100	4
20	secondary[2]	100	15
45	primary	100	27

[1] Primary indicates the aluminum containing surface directly exposed to the atmosphere and the test light.

[2] Secondary indicates the aluminum containing surface in physical contact with the glass. The light passed through the glass before being reflected from the secondary surface.

EXAMPLE 3

Aluminum flakes were formed by dissolving a TRYCITE (Trycite is a registered Trade Mark) plastic film substrate having a vacuum deposited aluminum coating thereon in a toluene solvent. The resulting mixture was pumped into a centrifuge to remove the liquid phase from the solid aluminum. The solid aluminum flakes were contacted with toluene to remove substantially all of the remaining substrate composition. The majority of flakes were determined to have a largest dimension of 300 to 400 microns with a minority having a largest dimension up to 1000 microns.

100 Grams of a slurry of the flakes in toluene (1.056 weight percent aluminum) was admixed with 31.7 grams of diethylbenzene, 48.7 grams of toluene and 30.6 grams of a solution of 30 milligrams/milliliter (mg/ml) of an ethylcellulose resin in toluene. This mixture was subjected to the sharp, rotating blade, of a standard kitchen blender for two minutes. The resulting mixture contained aluminum flakes of a reduced size. The majority of the flakes had a largest dimension of 100 microns with a minority being within a range of 10 to 20 microns.

The final aluminum flake containing mixture is suitable for use as a coating composition.

EXAMPLE 4

A paint containing 0.41 weight percent of about 350 angstrom thick aluminum flake was prepared by admixing together 50 cubic centimeters (cc) of toluene containing 310 milligrams (mg) of aluminum flake prepared in accord with present invention, 20 cc of toluene and 16 cc of a solution of a 100 centipoise ethylcellulose resin and toluene wherein the resin concentration in the toluene solution was 20 mg/ml of toluene. The aluminum in the paint was then subjected to a cutting, shear-type force to reduce the flake size by means of a kitchen blender.

The paint was sprayed onto an exterior surface of commercially available 25, 100 and 500 watt light bulbs. An adherent coating with a highly reflective secondary surface was obtained. The coatings on the light bulbs were use tested by alternately lighting and deenergizing the light bulbs for 15 minute periods. The coating on the 500 watt bulb began to blister after a test period of 24 hours, whereas, the coatings applied to the 25 and 100 watt bulbs remained in a satisfactory, undamaged condition after being tested for 10 days.

EXAMPLE 5

450 Angstrom thick flakes were produced in accord with the present invention from a substrate with a vapor deposited aluminum layer thereon. A sufficient amount of a toluene-1½ weight percent aluminum flake slurry was added to lacquers colored green, blue and brown (DuPont lacquer Nos. 5171, 5327 and 5425 respectively) to provide a flake concentration of about 0.25 grams of aluminum flake per gallon of final lacquer (gmAl/gal.) (0.066 grams/liter). Flake concentrations of about 0.5 gmAl/gal (0.132 grams Al/liter) of green and brown and about 1 gmAl/gal (0.264 grams Al/liter) of blue lacquer were also mixed.

Each of the aluminum containing lacquers was sprayed onto a primed 3 inch by 9 inch (7.62 centimeters by 22.82 centimeters) steel sheet and air dried. The sprayed and dried surfaces were compared to similar sheets sprayed with the same lacquer not having the aluminum flake added thereto. The aluminum flake containing green and brown coated surfaces had very good and the blue surfaces fair visual appearances with a greater metallic luster than the non-flake containing coated surfaces. An adherent flake containing coating, suitable for an automobile surface finsh resulted in each test specimen.

EXAMPLE 6

Magnesium, gold and silver were deposited by vacuum methods onto separate silicone resin type release agent coatings on MYLAR ("Mylar" is a registered Trade Mark) plastic films. The release agents were individually dissolved in toluene to form Mg, Au and Ag platelets and solid Mylar plastic film. The platelets were readily separated from the solid plastic film. The largest platelet dimesion of the Mg ranged from 200 to 3000 microns. The size range of the Au ranged from 50 to 600 microns. The Ag platelets had a largest dimension of from 400 to 5000 microns with the majority being within the range of 1000 to 2400 microns.

EXAMPLE 7

Copper platelets with the largest dimension being within the range of 40 to 3000 microns and the majority within the range of 200 to 2000 microns were formed by vacuum depositing copper on Trycite plastic film and then dissolving the plastic film in toluene.

EXAMPLE 8

In this experiment MYLAR ("Mylar" is a registered Trade Mark) plastic film is used as backing material. The film was coated with a silicone resin type release agent and then with a lacquer overcoating. An aluminum coating was vapor deposited on the lacquer surface. The coated film as described was immersed in a container of toluene. An ultrasonic probe was placed in the

toluene and activated for a period of about one minute. The ultrasonic vibration was provided by commercially available 150 watt equipment generating 25 kilohertz at full power by means of a magneto-strictive transducer. After about one minute of exposure to the ultrasonic-toluene environment at room temperature, a majority of the aluminum coating on the lacquer surface had been removed and was observed as a multiplicity of finely divided, platelet type particles sparkling with toluene.

EXAMPLE 9

Aluminum platelets were formed in accord with the present invention by immersing in toluene a one mil thick polystyrene film which had been vacuum coated with aluminum on two surfaces. Shiny aluminum platelets were released as the polystyrene dissolved.

WHAT WE CLAIM IS:—

1. A method for the preparation of particulate metal which method comprises depositing a metal coating on a substrate by vapor, electroless or sputter deposition and removing the metal coating from the substrate by dissolving the substrate in a solvent therefor, the thickness of the deposited coating being such that upon dissolution of the substrate the metal is released as a plurality of metal particles.

2. A method as claimed in claim 1 wherein the metal particles are separate irregularly shaped platelets.

3. A method as claimed in claim 2 wherein the metal is deposited by vapor deposition.

4. A method as claimed in claim 2 wherein the metal is deposited by electroless deposition.

5. A method as claimed in claim 3 or claim 4 wherein the substrate is a film.

6. A method as claimed in any one of claims 3 to 5 wherein each metal platelet is up to 1000 angstroms in thickness.

7. A method as claimed in any one of claims 3 to 5 wherein each metal platelet has a thickness of from 200 to 1000 angstroms.

8. A method as claimed in any one of claims 1 to 5 wherein each metal platelet has a thickness of from 350 to 600 angstroms.

9. A method as claimed in any one of claims 2 to 8 wherein the largest dimension of each metal platelet is from 1 to 5000 microns.

10. A method as claimed in any one of claims 2 to 8 wherein the largest dimension of each metal platelet is from 1 to 1200 microns.

11. A method as claimed in any one of claims 2 to 8 wherein the largest dimension of each metal platelet is from 100 to 1000 microns.

12. A method as claimed in any one of claims 2 to 11 wherein the metal coating is up to 1000 angstroms in thickness.

13. A method as claimed in any one of claims 8 to 12 wherein the metal is Mg, Al, Ni, Cu, Zn, Pd, Ag, Cd, Pt, Au or Pb.

14. A method as claimed in any one of claims 8 to 12 wherein the metal is aluminium.

15. A method as claimed in any one of claims 2 to 7 wherein the metal is Al, Ni, Cu, Zn, Pd, Ag, Cd, Pt, Au or Pb.

16. A method as claimed in any one of claims 2 to 7 wherein the metal is aluminium.

17. A method as claimed in any one of claims 8 to 14 wherein the substrate is a release layer interposed between the metal coating and a layer of material which is insoluble in the solvent for the substrate.

18. A method as claimed in any one of claims 8 to 14 and 17 wherein the substrate is a silicone resin.

19. A method as claimed in any one of claims 1 to 5 wherein the metal coating is removed from the substrate by contacting at least a portion of the metal coated substrate and subjecting the solvent and the metal coated substrate to ultrasonic vibration.

20. A method as claimed in claim 19 wherein the substrate is a release layer interposed between the metal coating and a layer of material which is insoluble in the solvent for the substrate.

21. A method as claimed in claim 20 wherein the release layer is a silicone resin layer.

22. A method as claimed in any one of claims 19 to 21 wherein the metal is Mg, Al, Ni, Cu, Zn, Pd, Ag, Cd, Pt, Au, or Pb.

23. A method as claimed in any one of claims 19 to 21 wherein the metal is aluminium.

24. A method for the preparation of particulate metal substantially as hereinbefore described in Example 8.

25. A method for the preparation of particulate metal substantially as hereinbefore described in any one of Examples 3 to 7 and 9.

26. A method for the preparation of particulate metal substantially as hereinbefore described in Example 1 or Example 2.

27. Particulate metal whenever prepared by a method as claimed in any one of claims 3 to 7, 15, 16 and 26.

28. Particulate metal whenever prepared by a method as claimed in any one of claims 1, 2, 8 to 14, 17, 18 and 26.

29. Particulate metal whenever prepared

by a method as claimed in any one of claims 19 to 24.

30. A coating composition comprising particulate metal as claimed in claim 27 and a carrier for the particulate metal.

31. A coating composition comprising particulate metal as claimed in claim 28 and a carrier for the particulate metal.

32. A coating composition as claimed in claim 31 wherein the particulate metal is present in an amount of from 0.1 to 10 weight percent based on the weight of the composition.

33. A coating composition as claimed in claim 31 wherein the particulate metal is present in an amount of from 0.1 to 5 weight percent based on the weight of the composition.

34. A coating composition comprising particulate metal as claimed in claim 29 and a carrier for the particulate metal.

35. A coating composition as claimed in claim 30 substantially as hereinbefore described in Example 1 or Example 2.

36. A coating composition as claimed in claim 31 substantially as hereinbefore described in any one of Examples 3 to 7 and 9.

37. A coating composition as claimed in claim 34 substantially as hereinbefore described in Example 8.

38. A method of coating an article which method comprises coating the article with a composition as claimed in claim 30 or claim 35.

39. A method of coating an article which method comprises coating the article with a composition as claimed in any one of claims 31 to 33 and 36.

40. A method of coating an article which method comprises coating the article with a composition as claimed in claim 34 or claim 37.

41. An article whenever prepared by a method as claimed in claim 38.

42. An article whenever prepared by a method as claimed in claim 39.

43. An article whenever prepared by a method as claimed in claim 40.

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